

CLAIMS

We Claim:

- 5 1. A method of polymerizing olefins, comprising:
 contacting ethylene and at least one olefin comonomer with a catalyst
 composition under polymerization conditions to form a copolymer;
 wherein the catalyst composition comprises the contact product of at least
 one tightly-bridged metallocene compound, at least one organoaluminum
10 compound, and at least one chemically-treated solid oxide;
 wherein the copolymer has a polydispersity index (Mw/Mn) less than or
equal to about 20; and
 wherein the copolymer has a film clarity of a 1 mil film less than or equal
to about 30%.
- 15 2. The method of Claim 1, wherein the polydispersity index is less
 than or equal to about 12, and the film clarity is less than or equal to about 20%.
- 20 3. The method of Claim 1, wherein the polydispersity index is less
 than or equal to about 10, and the film clarity is less than or equal to about 10%.
4. The method of Claim 1, wherein the copolymer is further
 characterized by a density less than about 0.935 g/cm³.
- 25 5. The method of Claim 1, wherein the copolymer is further
 characterized by a melt index (MI) from about 0.01 to about 10 dg/min.

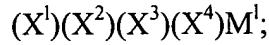
6 The method of Claim 1, wherein the copolymer is further characterized by a high load melt index (HLMI) from about 8 to about 180 dg/min.

5 7. The method of Claim 1, wherein the copolymer is further characterized by a film haze of a 1 mil film at least about 60%.

10 8. The method of Claim 1, wherein the copolymer is further characterized by a melt strength of a 1 mil film greater than or equal to about 5.0 in.

9. The method of Claim 1, wherein the copolymer is further characterized by a 1% MD Secant modulus of less than about 50,000 psi.

15 10. The method of Claim 1, wherein the tightly-bridged metallocene compound is selected from a compound having the following formula:



wherein M¹ is selected from titanium, zirconium, or hafnium;

20 wherein (X¹) and (X²) are independently selected from a cyclopentadienyl, an indenyl, or a fluorenyl, any one of which can be substituted or unsubstituted; wherein (X¹) and (X²) are connected by a substituted or unsubstituted bridging group comprising:

a) one atom selected from carbon, silicon, germanium, or tin, bonded to both (X¹) and (X²); or

b) two contiguous carbon atoms in a chain, one end of which is bonded to (X¹) and the other end of which is bonded to (X²); and wherein (X³); (X⁴); each substituent on the substituted cyclopentadienyl, the substituted indenyl, and the substituted fluorenyl; and each substituent on the substituted bridging group are independently selected from a hydrocarbyl group,

an aliphatic group, an aromatic group, a cyclic group, a combination of aliphatic and cyclic groups, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted derivative thereof, having from 1 to about 30 carbon atoms; a halide; or hydrogen.

11. The method of Claim 1, wherein the tightly-bridged metallocene compound is selected from a compound having the following formula:

$$10 \hspace{10cm} (X^1)(X^2)(X^3)(X^4)M^1;$$

wherein M¹ is selected from Zr or Hf;

wherein (X¹) and (X²) are independently selected from a cyclopentadienyl, an indenyl, or a fluorenyl, any one of which can be substituted or unsubstituted;

wherein (X¹) and (X²) are connected by a bridging group selected from >CR¹₂, >SiR¹₂, or -CR¹₂CR¹₂-, wherein R¹ in each instance is independently selected from a linear, branched, substituted, or unsubstituted hydrocarbyl group, any one of which having from 1 to about 30 carbon atoms; or hydrogen; and

wherein any substituent on (X¹), (X²), or R¹ is independently selected from a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an inorganic group, an organometallic group, having from 1 to about 30 carbon atoms; a halide; or hydrogen; and

wherein (X³); (X⁴) are independently selected from alkoxide or aryloxide having from 1 to about 30 carbon atoms, halide, or hydride.

25 12. The method of Claim 1, wherein the tightly-bridged metallocene
compound is selected from:

rac-1,2-ethanediylbis(η^5 -1-indenyl)dichlorozirconium;

1,2-ethanediylbis(η^5 -1-indenyl)di-n-butoxyhafnium;

1,2-ethanediylbis(η^5 -1-indenyl)dimethylzirconium;

3,3-pentanediylibis(η^5 -4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride;
methylphenylsilylibis(η^5 -4,5,6,7-tetrahydro-1-indenyl)zirconium
dichloride;

rac-dimethylsilylibis(1-indenyl)zirconium dichloride;

5 octylphenylsilylibis(1-indenyl)hafnium dichloride; or
dimethylsilylibis(η^5 -4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride.

rac-dimethylsilylibis(2-methyl-1-indenyl)zirconium dichloride;

1,2-ethanediylbis(9-fluorenyl)zirconium dichloride;

methyloctylsilylibis(9-fluorenyl)zirconium dichloride;

10 diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride;

diphenylmethylidene(cyclopentadienyl)(indenyl)zirconium dichloride;

iso-propylidenebis(cyclopentadienyl)zirconium dichloride;

iso-propylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

iso-propylidene(3-methylcyclopentadienyl)(9-fluorenyl)zirconium
15 dichloride;

meso-ethylenebis(1-indenyl)zirconium dichloride;

rac-ethylenebis(2-methyl-1-indenyl)zirconium dichloride;

rac-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride;

dimethylsilylibis(cyclopentadienyl)zirconium dichloride;

20 dimethylsilylibis(9-fluorenyl)zirconium dichloride;

meso-dimethylsilylibis(2-methylindenyl)zirconium dichloride;

rac-dimethylsilylibis(tetrahydroindenyl) zirconium dichloride;

dimethylsilylibis(tetramethylcyclopentadienyl) zirconium dichloride;

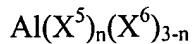
diphenylsilyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

25 diphenylsilylibis(indenyl)hafnium dichloride; or
any combination thereof.

13. The method of Claim 1, wherein the tightly-bridged metallocene compound is selected from *rac*-1,2-ethanediylbis(η^5 -1-

indenyl)dichlorozirconium, dimethylsilyl*bis*(indenyl)zirconium dichloride, or a combination thereof.

14. The method of Claim 1, wherein the organoaluminum compound
5 comprises a compound with the formula:



wherein (X^5) is a hydrocarbyl having from 1 to about 20 carbon atoms; (X^6) is selected from alkoxide or aryloxide having from 1 to about 20 carbon atoms, halide, or hydride; and n is a number from 1 to 3, inclusive.

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15. The method of Claim 1, wherein, the the organoaluminum compound comprises trimethylaluminum (TMA), triethylaluminum (TEA), tripropylaluminum, diethylaluminum ethoxide, tributylaluminum, diisobutylaluminum hydride, triisobutylaluminum, diethylaluminum chloride, or
15 any combination thereof.

20 16. The method of Claim 1, wherein the chemically-treated solid oxide comprises a material selected from fluorided silica-alumina, fluorided alumina, fluorided silica-titania, fluorided silica-zirconia, chlorided zinc-aluminum oxide, sulfated alumina, or any combination thereof.

25 17. The method of Claim 1, wherein the tightly-bridged metallocene compound comprises *rac*-ethylene*bis*(indenyl)zirconium dichloride or dimethylsilyl*bis*(indenyl)zirconium dichloride, the organoaluminum compound comprises triethylaluminum, and the chemically-treated solid oxide comprises fluorided silica-alumina.

18. The method of Claim 1, wherein the contacting is conducted in the presence of a diluent comprising isobutane.

19. The method of Claim 1, wherein the catalyst composition further comprises the contact product of an optional cocatalyst selected from at least one aluminoxane, at least one organozinc compound, at least one organoboron compound, at least one ionizing ionic compound, or any combination thereof.

20. A method of polymerizing olefins, comprising:
contacting ethylene and at least one olefin comonomer with a catalyst composition under polymerization conditions to form a copolymer;

10 wherein the catalyst composition comprises the contact product of at least one tightly-bridged metallocene compound, at least one organoaluminum compound, and at least one chemically-treated solid oxide;
 wherein the copolymer has a film haze of a 1 mil film at least about 60%;
and
15 wherein the copolymer has a high load melt index (HLMI) from about 8 to about 180 dg/min.

21. The method of Claim 20, wherein the film haze of a 1 mil film is at least about 70%, and high load melt index is from about 10 to about 150 dg/min.

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22. The method of Claim 20, wherein the film haze of a 1 mil film is at least about 70%, and the high load melt index is from about 11 to about 100 dg/min.

25 23. The method of Claim 20, wherein the copolymer is further characterized by a polydispersity index (Mw/Mn) less than or equal to about 20.

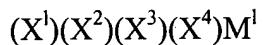
24. The method of Claim 20, wherein the copolymer is further characterized by a density less than about 0.935 g/cm³.

25. The method of Claim 20, wherein the copolymer is further characterized by a melt index (MI) from about 0.01 to about 10 dg/min.

5 26. The method of Claim 20, wherein the copolymer is further characterized by a melt strength of a 1 mil film greater than or equal to about 5.0 in.

10 27. The method of Claim 20, wherein the copolymer is further characterized by a 1% MD Secant modulus of less than about 50,000 psi.

28. The method of Claim 20, wherein the tightly-bridged metallocene compound is selected from a compound having the following formula:



15 wherein M^1 is selected from titanium, zirconium, or hafnium;

wherein (X^1) and (X^2) are independently selected from a cyclopentadienyl, an indenyl, or a fluorenyl, any one of which can be substituted or unsubstituted;

wherein (X^1) and (X^2) are connected by a substituted or unsubstituted bridging group comprising:

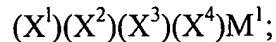
20 a) one atom selected from carbon, silicon, germanium, or tin, bonded to both (X^1) and (X^2) ; or

b) two contiguous carbon atoms in a chain, one end of which is bonded to (X^1) and the other end of which is bonded to (X^2) ; and wherein (X^3) ; (X^4) ; each substituent on the substituted cyclopentadienyl,

25 the substituted indenyl, and the substituted fluorenyl; and each substituent on the substituted bridging group are independently selected from a hydrocarbyl group, an aliphatic group, an aromatic group, a cyclic group, a combination of aliphatic and cyclic groups, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium

group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted derivative thereof, having from 1 to about 30 carbon atoms; a halide; or hydrogen.

5 29. The method of Claim 20, wherein the tightly-bridged metallocene compound is selected from a compound having the following formula:



wherein M^1 is selected from Zr or Hf;

10 wherein (X^1) and (X^2) are independently selected from a cyclopentadienyl, an indenyl, or a fluorenyl, any one of which can be substituted or unsubstituted; wherein (X^1) and (X^2) are connected by a bridging group selected from $>CR^1_2$, $>SiR^1_2$, or $-CR^1_2CR^1_2-$, wherein R^1 in each instance is independently selected from a linear, branched, substituted, or unsubstituted hydrocarbyl group, any one of which having from 1 to about 30 carbon atoms; or hydrogen; and
15 wherein any substituent on (X^1) , (X^2) , or R^1 is independently selected from a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an inorganic group, an organometallic group, having from 1 to about 30 carbon atoms; a halide; or hydrogen; and
20 wherein (X^3) ; (X^4) are independently selected from alkoxide or aryloxide having from 1 to about 30 carbon atoms, halide, or hydride.

30. The method of Claim 20, wherein the tightly-bridged metallocene compound is selected from:

rac-1,2-ethanediylbis(η^5 -1-indenyl)dichlorozirconium;
25 1,2-ethanediylbis(η^5 -1-indenyl)di-n-butoxyhafnium;
1,2-ethanediylbis(η^5 -1-indenyl)dimethylzirconium;
3,3-pantanediylbis(η^5 -4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride;
methylphenylsilylbis(η^5 -4,5,6,7-tetrahydro-1-indenyl)zirconium
dichloride;

rac-dimethylsilylbis(1-indenyl)zirconium dichloride;
octylphenylsilylbis(1-indenyl)hafnium dichloride; or
dimethylsilylbis(η^5 -4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride.

5 *rac*-dimethylsilylbis(2-methyl-1-indenyl)zirconium dichloride;
1,2-ethanediylbis(9-fluorenyl)zirconium dichloride;
methyloctylsilylbis(9-fluorenyl)zirconium dichloride;
diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride;
diphenylmethylidene(cyclopentadienyl)(indenyl)zirconium dichloride;
iso-propylidenebis(cyclopentadienyl)zirconium dichloride;

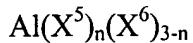
10 *iso*-propylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
iso-propylidene(3-methylcyclopentadienyl)(9-fluorenyl)zirconium
dichloride;
meso-ethylenebis(1-indenyl)zirconium dichloride;
rac-ethylenebis(2-methyl-1-indenyl)zirconium dichloride;

15 *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride;
dimethylsilylbis(cyclopentadienyl)zirconium dichloride;
dimethylsilylbis(9-fluorenyl)zirconium dichloride;
meso-dimethylsilylbis(2-methylindenyl)zirconium dichloride;
rac-dimethylsilylbis(tetrahydroindenyl) zirconium dichloride;

20 dimethylsilylbis(tetramethylcyclopentadienyl) zirconium dichloride;
diphenylsilyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
diphenylsilylbis(indenyl)hafnium dichloride; or
any combination thereof.

25 31. The method of Claim 20, wherein the tightly-bridged metallocene compound is selected from *rac*-1,2-ethanediylbis(η^5 -1-indenyl)dichlorozirconium, dimethylsilylbis(indenyl)zirconium dichloride, or a combination thereof.

32. The method of Claim 20, wherein the organoaluminum compound comprises a compound with the formula:



wherein (X^5) is a hydrocarbyl having from 1 to about 20 carbon atoms; (X^6) is

5 selected from alkoxide or aryloxide having from 1 to about 20 carbon atoms, halide, or hydride; and n is a number from 1 to 3, inclusive.

33. The method of Claim 20, wherein the the organoaluminum compound comprises trimethylaluminum (TMA), triethylaluminum (TEA),
10 tripropylaluminum, diethylaluminum ethoxide, tributylaluminum, diisobutylaluminum hydride, triisobutylaluminum, diethylaluminum chloride, or any combination thereof.

34. The method of Claim 20, wherein the chemically-treated solid
15 oxide comprises a material selected from fluorided silica-alumina, fluorided alumina, fluorided silica-titania, fluorided silica-zirconia, chlorided zinc-aluminum oxide, sulfated alumina, or any combination thereof.

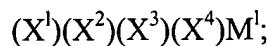
35. The method of Claim 20, wherein the tightly-bridged metallocene
20 compound comprises *rac*-ethylenebis(indenyl)zirconium dichloride or dimethylsilylbis(indenyl)zirconium dichloride, the organoaluminum compound comprises triethylaluminum, and the chemically-treated solid oxide comprises fluorided silica-alumina.

25 36. The method of Claim 20, wherein the contacting is conducted in the presence of a diluent comprising isobutane.

37. The method of Claim 20, wherein the catalyst composition further comprises the contact product of an optional cocatalyst selected from at least one

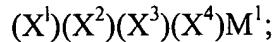
aluminoxane, at least one organozinc compound, at least one organoboron compound, at least one ionizing ionic compound, or any combination thereof.

38. A composition comprising the contact product of at least one
5 tightly-bridged metallocene compound, at least one organoaluminum compound, and at least one chemically-treated solid oxide, wherein the tightly-bridged metallocene compound is selected from a compound having the following formula:



10 wherein M^1 is selected from titanium, zirconium, or hafnium; wherein (X^1) and (X^2) are independently selected from a cyclopentadienyl, an indenyl, or a fluorenyl, any one of which can be substituted or unsubstituted; wherein (X^1) and (X^2) are connected by a substituted or unsubstituted bridging group comprising:
15 a) one atom selected from carbon, silicon, germanium, or tin, bonded to both (X^1) and (X^2) ; or
b) two contiguous carbon atoms in a chain, one end of which is bonded to (X^1) and the other end of which is bonded to (X^2) ; and wherein (X^3) ; (X^4) ; each substituent on the substituted cyclopentadienyl,
20 the substituted indenyl, and the substituted fluorenyl; and each substituent on the substituted bridging group are independently selected from a hydrocarbyl group, an aliphatic group, an aromatic group, a cyclic group, a combination of aliphatic and cyclic groups, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an arsenic group, a carbon group, a silicon group, a germanium group, a tin group, a lead group, a boron group, an aluminum group, an inorganic group, an organometallic group, or a substituted derivative thereof, having from 1
25 to about 30 carbon atoms; a halide; or hydrogen.

39. The composition of Claim 38, wherein the tightly-bridged metallocene compound is selected from a compound having the following formula:



5 wherein M¹ is selected from Zr or Hf;

 wherein (X¹) and (X²) are independently selected from a cyclopentadienyl, an indenyl, or a fluorenyl, any one of which can be substituted or unsubstituted;

 wherein (X¹) and (X²) are connected by a bridging group selected from >CR¹₂, >SiR¹₂, or -CR¹₂CR¹₂-, wherein R¹ in each instance is independently

10 selected from a linear, branched, substituted, or unsubstituted hydrocarbyl group, any one of which having from 1 to about 30 carbon atoms; or hydrogen; and

 wherein any substituent on (X¹), (X²), or R¹ is independently selected from a hydrocarbyl group, an oxygen group, a sulfur group, a nitrogen group, a phosphorus group, an inorganic group, an organometallic group, having from 1 to about 30 carbon atoms; a halide; or hydrogen; and

15 wherein (X³); (X⁴) are independently selected from alkoxide or aryloxide having from 1 to about 30 carbon atoms, halide, or hydride.

40. The composition of Claim 38, wherein the tightly-bridged
20 metallocene compound is selected from:

rac-1,2-ethanediylbis(η^5 -1-indenyl)dichlorozirconium;

1,2-ethanediylbis(η^5 -1-indenyl)di-n-butoxyhafnium;

1,2-ethanediylbis(η^5 -1-indenyl)dimethylzirconium;

3,3-pantanediylbis(η^5 -4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride;

25 methylphenylsilylbis(η^5 -4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride;

rac-dimethylsilylbis(1-indenyl)zirconium dichloride;

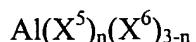
octylphenylsilylbis(1-indenyl)hafnium dichloride; or

dimethylsilylbis(η^5 -4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride.

rac-dimethylsilylbis(2-methyl-1-indenyl)zirconium dichloride;
1,2-ethanediylbis(9-fluorenyl)zirconium dichloride;
methyloctylsilylbis(9-fluorenyl)zirconium dichloride;
diphenylmethyldene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride;
5 diphenylmethyldene(cyclopentadienyl)(indenyl)zirconium dichloride;
iso-propylidenebis(cyclopentadienyl)zirconium dichloride;
iso-propylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
iso-propylidene(3-methylcyclopentadienyl)(9-fluorenyl)zirconium
dichloride;
10 *meso*-ethylenebis(1-indenyl)zirconium dichloride;
rac-ethylenebis(2-methyl-1-indenyl)zirconium dichloride;
rac-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride;
dimethylsilylbis(cyclopentadienyl)zirconium dichloride;
dimethylsilylbis(9-fluorenyl)zirconium dichloride;
15 *meso*-dimethylsilylbis(2-methylindenyl)zirconium dichloride;
rac-dimethylsilylbis(tetrahydroindenyl) zirconium dichloride;
dimethylsilylbis(tetramethylcyclopentadienyl) zirconium dichloride;
diphenylsilyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
diphenylsilylbis(indenyl)hafnium dichloride; or
20 any combination thereof.

41. The composition of Claim 38, wherein the tightly-bridged metallocene compound is selected from *rac*-1,2-ethanediylbis(η^5 -1-indenyl)dichlorozirconium, dimethylsilylbis(indenyl)zirconium dichloride, or a combination thereof.
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42. The composition of Claim 38, wherein the organoaluminum compound comprises a compound with the formula:



wherein (X⁵) is a hydrocarbyl having from 1 to about 20 carbon atoms; (X⁶) is selected from alkoxide or aryloxide having from 1 to about 20 carbon atoms, halide, or hydride; and n is a number from 1 to 3, inclusive.

5 43. The composition of Claim 38, wherein, the the organoaluminum compound comprises trimethylaluminum (TMA), triethylaluminum (TEA), tripropylaluminum, diethylaluminum ethoxide, tributylaluminum, diisobutylaluminum hydride, triisobutylaluminum, diethylaluminum chloride, or any combination thereof.

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44. The composition of Claim 38, wherein the chemically-treated solid oxide comprises a material selected from fluorided silica-alumina, fluorided alumina, fluorided silica-titania, fluorided silica-zirconia, chlorided zinc-aluminum oxide, sulfated alumina, or any combination thereof.

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45. The composition of Claim 38, wherein the tightly-bridged metallocene compound comprises *rac*-ethylenebis(indenyl)zirconium dichloride or dimethylsilylbis(indenyl)zirconium dichloride, the organoaluminum compound comprises triethylaluminum, and the chemically-treated solid oxide comprises fluorided silica-alumina.

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